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(54) Title of the Invention:

ABRASION-RESISTANT AND OXIDATION-RESISTANT
COATING FOR SiC BODIES

(57) Abstract:

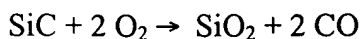
After a suspension of a polysiloxane and molybdenum disilicide, which may contain a solvent, has been applied to a porous silicon carbide body, the following process steps are used to produce an erosion-resistant protective coating that protects the substrate body from oxidation at temperatures up to 1,700°C: crosslinking of the polysiloxane phase at temperatures up to a maximum of 400°C, reaction pyrolysis in an oxygen-free atmosphere at 1,000-1,600°C, and a subsequent heat treatment at temperatures above 800°C, and preferably at temperatures of 1,400-1,700°C, in an atmosphere that contains oxygen. In addition to molybdenum disilicide, the suspension used for the coating may also contain substances from the following group: silicon carbide, silicides of the metals niobium, tantalum, chromium, tungsten, and aluminum, and alumina formers.

SPECIFICATION

The invention concerns an abrasion-resistant surface coating, which protects substrate bodies made of porous silicon carbide from oxidation by oxygen and contains a matrix glass, silicon carbide, and molybdenum disilicide, and a method of producing this coating.

Due to their strength, oxidation resistance, and creep resistance at high temperatures, parts made of silicon carbide (SiC) are used for heating, supporting, protective, and construction purposes in high-temperature systems. Examples are heating elements, susceptors, crucibles, thermometer wells, radiation shields, baffle plates and deflectors, support frames, and rollers for many different types of furnaces in industry and the laboratory. The creep strength of such parts made of porous, sintered, reaction-bonded or recrystallized SiC types is on the order of 1,500°C. At higher temperatures, stability decreases, since the silicon dioxide layer, which initially forms

by the action of atmospheric oxygen according to the equation



and protects the entire gas-accessible surface from oxidation, is damaged by continuous release of gaseous silicon suboxide phases (SiO) and thus can no longer perform its protective function. Therefore, the use of silicon carbide parts at still higher temperatures in an oxidizing atmosphere requires more stable protective coatings, which either cover the entire gas-accessible pore system of the bodies or reliably seal the entire external surface, including the pore openings. There have been repeated attempts to make such protective coatings available. Molybdenum disilicide (MoSi_2) often appears as an important constituent of these protective coatings.

According to German Auslegeschrift [*Late Disclosure*] No.11 42 042, the oxidation resistance of SiC heating conductors is increased by first covering their surface with a coating of molybdenum disilicide and then converting this coating to a glassy, oxidation-resistant coating that contains molybdenum, silicon, oxygen, and in some cases carbon by calcining at temperatures of 1,300-1,500°C. In the later patent DE 14 96 660, questions are again raised about the effectiveness of protective coatings produced in this way. These coatings would still have pores, which would allow oxidizing gases to enter. To overcome these difficulties, the later patent proposes that a dense coating that protects against oxidation be produced from a glass that is made from silicon dioxide, aluminum oxide, alkaline-earth oxide, and alkali oxide and contains a metal silicide. The incorporated silicide, e.g., MoSi_2 , is meant to act as a getter in the coating and to bind oxygen that diffuses into the coating by reaction to exclusively nonvolatile reaction products, mainly SiO_2 . DE 40 34 001 A1 discloses another type of protective coating for substrates that consist essentially of carbon. This protective coating contains molybdenum disilicide and a low-melting matrix, such as a glass or a glass ceramic, as a component that

reduces mechanical stresses at high temperatures.

The chief problem with the use of molybdenum disilicide-containing protective coatings with glass matrices is the resistance to thermal shock of the materials involved in the given technical solution. During continuous changes from high temperatures, which are understood here to mean temperatures of 1,700-1,750°C, to room temperature, demands are placed on the interfaces between substrate and protective coating that effect adhesion, which cannot always be met due to different substance characteristics, especially different coefficients of thermal expansion. This then results in coating separation and cracks in the cooled state. Damage of this type occurs especially when the interfaces that effect the adhesion are exposed to additional mechanical stresses due to mechanical loads placed on parts, e.g., when material that is to be heat-treated in a furnace is placed on these parts. When reheating to working temperatures occurs, the coating cannot be sufficiently restored to its undamaged state, if indeed any restoration at all is possible, and the substrate body is then damaged. Another requirement that is placed on oxidation-resistant coatings that can withstand large thermal stresses is resistance to erosion, which is inadequate, if the coatings soften to a relatively great extent at high temperatures, e.g., if they contain glasses that contain alkali metals or alkaline-earth metals and they do not contain substances that are sufficiently resistant to abrasion.

Therefore, the objective of the invention was to create oxidation-resistant coatings for porous parts made of silicon carbide, which adhere strongly to the substrate bodies, exhibit long-term thermal stability up to temperatures of 1,700°C, and, in addition, are resistant to erosion. A further objective of the invention was to specify a method of producing coatings of this type.

These objectives are achieved by the features of the characterizing clauses of Claims 1 and 5 [*sic; apparently, "Claims 1 and 4" was intended, since Claim 4 is the independent claim*

with respect to the method of the invention -- Tr. Ed.]. The claims that are dependent on Claims 1 and 5 [*sic -- Tr. Ed.*], which are herewith introduced into the specification, are preferred embodiments of the invention.

An essential feature of the solution of the invention is the use of polysiloxanes as intermediate products for the production of a matrix glass that contains, among other components, silicon carbide. As the silicon carbide phases are forming from the siloxane, they also grow by epitaxy on the substrate, which likewise consists of silicon carbide. This effect, in conjunction with the other anchoring effects of a glass melt on a porous surface, produces especially good adhesion. The substrate may have any desired shape, and may be formed, for example, as a plate, block, tube, crucible, rod, or fretwork.

Polymeric organosilicon compounds, such as siloxanes, have already been successfully used for the production of ceramic fibers, powders, and wear-resistant coatings. However, due to the enormous increase in density of more than 100% that occurs during the pyrolytic polymer/ceramic transformation and the associated volume contraction of up to 80%, parts or coatings with a high density could not be obtained. Only by the incorporation of reactive filler powders in the polymer matrix did it finally become possible to reduce the contraction that occurs during the transformation to the ceramic state to such an extent that larger parts could be produced (EP 0 412 428 B1). Although composite materials obtained in this way are distinguished by their low contraction values, they are openly porous. The essence of the invention then is to mix a polysiloxane resin in liquid form with finely powdered molybdenum disilicide as a reactive filler until a suspension is produced, to coat a porous substrate body made of silicon carbide with this suspension, and then to carry out a heat treatment to convert this coating to a cohesive, practically gastight and thus oxidation-resistant coating that consists of a

composite material. This occurs by first removing vaporizable substances, such as water or solvent, from the coating by raising the temperature slightly and/or by applying a vacuum. The polysiloxane is then thermally crosslinked in the temperature range up to a maximum of 400°C. The part is then pyrolyzed in a nonoxidizing atmosphere, e.g., in argon or nitrogen, at temperatures of 1,000-1,500°C, which results in the escape of hydrogen, low hydrocarbons, and small amounts of CO as pyrolysis products. The pyrolysis leads essentially to the formation of an Si-O-C matrix glass, in which MoSi₂ is incorporated, and which, to a certain extent, may contain carbidic phases as well as nitridic phases, if nitrogen was used as the surrounding atmosphere during the reaction pyrolysis step. Since the nitridic phases are not as resistant to high temperatures as the other components mentioned above, if a nitrogen atmosphere is used, the reaction pyrolysis should not be carried out at temperatures above 1,250°C to avoid the formation of appreciable amounts of nitridic phases. The molybdenum disilicide and the carbidic phases, together with the Si-O-C matrix glass, are responsible for the resistance to high temperatures, the corrosion resistance, and the oxidation resistance of the protective coating. If, in addition to molybdenum disilicide, other ceramic silicon compounds or phases or aluminum-containing compounds or phases are present in the applied coating, they may likewise participate in the reactions that take place in the process steps carried out at high temperatures. The glassy coating produced in this way just contains more pores and cracks that are smaller than 10 μm. This residual porosity is sealed by a subsequent heat treatment in air at minimum temperatures of 800°C and preferably at temperatures of 1,500-1,700°C. At the high temperatures that prevail in the reaction pyrolysis and the vitrification step, a portion of the MoSi₂ may also be converted to Mo₂C and SiC by reaction with the carbon present in the matrix glass. The remainder of the filler phase is present as unreacted MoSi₂ or as Mo₅Si₃ in the composite material formed in this

way. These substances, especially the molybdenum disilicide, the silicon carbide, and the Si-O-C phase formed from the siloxane produce the outstanding combination of properties of this coating: oxidation resistance, coating stability, and abrasion resistance.

The last heat treatment under oxidizing conditions does not have to be carried out immediately after the ceramization process. It is also possible to carry it out during the first stipulated heating of the body coated with the vitrified coating to working temperature in an oxidizing atmosphere.

A protective coating produced by the method described above is also an object of the invention.

The pyrolysis of siloxanes to products that contain silicon carbide is well known. For more information on this subject, see, for example, White et al., Preparation of Silicon Carbide from Organosilicon Gels, Parts I and II, *Advanced Ceramic Materials*, Vol. 2, No. 1 [1987], pp. 45-59. The preparation of suitable polysiloxane gels is also described there. However, suitable polysiloxane formulations can also be obtained from the well-known manufacturers of organosilicon compounds. Siloxane resins crosslinked by both condensation and addition polymerization are suitable as starting materials for the production of coatings in accordance with the invention. The siloxanes that are used may have a large number of organic ligands, for example, alkyl, aryl, and especially phenyl or alkoxy groups. In accordance with a preferred embodiment of the invention, siloxane resins are used, whose yield of ceramic residue after the thermal decomposition is at least 70 wt.%. This group includes silsesquioxanes, e.g., $(\text{RSiO}_{1.5})_n$, with ligands R, such as the vinyl, allyl, or phenyl group, which are either highly reactive or have a high carbon content or have both of these characteristics. The low-viscosity siloxane formulations can be mixed directly with the finely powdered fillers, and the mixture can then be

applied to the substrate surfaces. Higher-viscosity gels are adjusted to the desired viscosity with a suitable solvent. Solvents are also used for dilution if the viscosity of the mixtures of polysiloxane and filler has become too high. To improve the wetting of the substrate by the applied suspension and to improve the adhesion of the coating on the substrate, the surface of the parts to be coated is preferably coated with a silane coupling agent.

The substrates to be coated contain 10-60, and preferably 20-50 vol.%, of finely pulverized molybdenum disilicide, based on the siloxane phase = 100 vol.%.

To improve the abrasion resistance and further adjust the thermal expansion of the ceramic coating, additional components in finely powdered form may be added to the suspension. The use of substances that contain silicon, such as SiC, CrSi₂, TaSi₂, NbSi₂, or WSi₂, is preferred for this purpose. They are added to the suspension in additional amounts of up to 60 vol.%, based on the suspension before the addition of these additives = 100 vol.%.

Additives of this type generally also act to improve the adhesion of the coating on the substrate.

The admixture of additives that form aluminum oxide or aluminosilicate glass is especially advantageous with respect to the oxidation-inhibiting effect of the protective coating. Suitable additives of this type include aluminides, e.g., AlSi, AlZr alloys, or aluminum silicide (Al₄Si₃) or mullite or hydroxides, for example, boehmite or hydrargillite, which form a partially crystalline protective coating that is resistant to high temperatures by reactive combination with the silicide fillers in an oxidizing atmosphere.

The suspension may be applied to the substrate by any of the well-known methods, i.e., for example, by dipping in the suspension, by spreading the suspension on with brushes or rollers, by spraying the suspension, or, if deeper penetration of the suspension into the pores of the body is intended, by a vacuum-pressure treatment of the substrate body immersed in the

suspension. The consistency of the suspension can be adapted to the particular application method that is used by dilution with suitable solvents, such as toluene, acetone, or trichloromethane. These solvents must be drawn off, i.e., removed in gaseous form, by methods that are well known to anyone skilled in the art after the application of the coating and before the beginning of the chemical crosslinking reaction.

Surface coatings in accordance with the invention serve as coatings on porous substrate bodies made of silicon carbide, which are resistant to abrasion, high temperatures, and oxidation at temperatures of up to 1,700°C. Suitable porous substrates of this type include especially molded parts made of sintered, reaction-bonded, or recrystallized silicon carbide.

The invention is explained below with reference to specific embodiments.

Example 1

A mixture of a polymethyl silsesquioxane (type NH 2100, Chemiewerke Nünchritz), which contained 40 vol.% of an MoSi₂ powder of an intermediate particle size $d_{50} = 3 \mu\text{m}$ (type grade C, from H. C. Starck Co., Goslar), was converted to a homogeneous suspension with a viscosity approximately the same as that of water at 20°C by intensive mixing with the addition of acetone as solvent. A plate with the dimensions $5 \times 5 \times 1 \text{ cm}$, which was composed of reaction-sintered silicon carbide with a pore volume of 16% and a mean pore diameter of ca. $30 \mu\text{m}$, was repeatedly immersed in this suspension at standard pressure until a suspension coating ca. $100 \mu\text{m}$ thick had been applied. The adhering solvent was removed by gentle heating after each immersion step. The plate was then heated to 180°C within 3 hours in air in a drying cabinet and left at this temperature for an additional 4 hours to complete the crosslinking of the siloxane. The plate was then transferred to a protective atmosphere furnace, heated in the

furnace to 1,200°C within 10 hours in an argon atmosphere, and left at this end temperature for one additional hour to complete the pyrolysis. The resulting ceramic composite coating consisted of an amorphous Si-O-C matrix phase in which MoSi₂ and SiC particles were embedded. This coating was firmly anchored in the surface of the substrate body and was already largely gastight. In the subsequent aging treatment in air at 1,600°C for a period of 10 hours, no weight change due to oxidation was observed.

Example 2

A high-speed stirrer was used to prepare a suspension with a viscosity similar to that of water from 100 parts by volume of polymethyl silsesquioxane (same type as in Example 1), 25 parts by volume of MoSi₂ (same type as in Example 1), and 25 parts by volume of CrSi₂, mean particle size 1.8 μm (by FSSS, manufacturer H. C. Starck Co., Goslar), with the addition of 90 wt.% acetone, based on the mixture of polysiloxane, MoSi₂, and CrSi₂ = 100 wt.%. The part to be coated in this example was a length of pipe made of reaction-sintered silicon carbide with the following dimensions: 15-mm outside diameter, 11-mm inside diameter, and 150-mm length, which had a pore volume of 16% and a mean pore diameter of 30 μm. Before the surface of the pipe was coated with the suspension, the pipe was coated with a silane coupling agent (type VTMO, Chemiewerke Hüls). This measure was designed to further improve the coupling of the functional groups of the polysiloxane to the SiC surface of the substrate. The coating of coupling agent was applied by dipping the pipe and then drying it in air for half an hour at 50°C. The prepared suspension was then applied by repeated immersion until a coating thickness of 150 μm had been produced. After the solvent had been removed, the temperature was slowly raised (ca. 1 K/min) to 180°C, and then the polysiloxane component of the coating was

crosslinked for 3 hours at temperatures of 180-220°C. The reaction pyrolysis was then carried out at 1,500°C in a nitrogen atmosphere [*N.b. The author(s) may have mixed up the values in Examples 2 and 3. In Example 2, they state 1,500°C in a nitrogen atmosphere, and in Example 3, they state 1,250°C in an argon atmosphere. This conflicts with their earlier advisory about not heating above 1,250°C when the reaction pyrolysis is carried out in nitrogen -- Tr. Ed.*] with a residence time of 4 hours. The ceramic protective coating obtained in this way consisted of a mixture of Si₃N₄, Mo₂C, MoSi₂, Cr₃C₂, and SiC. These substances were embedded in the matrix glass. The body produced in this way showed no weight loss due to oxidation after treatment at 1,500°C in air.

Example 3

A mixture of 100 vol.% polyphenylmethylsiloxane (type H62C, Wacker Chemie Co.) and 30 vol.% MoSi₂ powder (same type as in Example 1), and 10 vol.% Al₄Si₃ (maximum particle size 150 μm, Goodfellow, Bad Nauheim) was worked into a suspension with a water-like consistency with the use of trichloromethane as solvent. This suspension was sprayed with a spray gun onto a plate with the dimensions 10 × 10 × 1 cm, which was composed of reaction-sintered silicon carbide, and then the applied coating was dried. The process was repeated until a coating thickness of ca. 50 μm was obtained. The thermal crosslinking of the polymer was carried out as described in Examples 1 and 2 at a temperature of 200°C. This was followed, likewise in the basically prescribed way, by the reaction pyrolysis, which was carried out in this example at 1,250°C in an argon atmosphere. The plate that had been coated in this way was then subjected to a heat treatment at a heating rate of 2 K/minute from 1,200 to 1,600°C. The surface-tight [*surface-dense?; We suppose they mean "The gastight protective coating " -- Tr. Ed.*]

protective coating formed in this way consisted of the matrix phase as well as an aluminosilicate glass and crystalline mullite ($\text{Al}_2\text{O}_3 \times \text{SiO}_2$). It was resistant to oxidation, i.e., its weight was constant, up to temperatures of 1,600°C.

Example 4

An SiC pipe of the type described in Example 2 was immersed in an evacuated vessel filled with a highly fluid suspension (viscosity similar to that of water) of a polysiloxane and MoSi_2 , synthetic mullite (VAW Aluminium AG, Schwandorf), particle size 0 to 0.1 mm, and aluminum silicide (same type as in Example 3). The vessel was then evacuated to a pressure of $< 10^2$ Pa and maintained at this pressure for ca. 5 minutes. The vessel was then repressurized. This forced the suspension into the pores of the pipe to a depth of ca. 2 mm from the surface of the molded part. After the pipe had been removed from the suspension, it was subjected to the treatment conditions described in Example 3 to crosslink and pyrolyze the applied coating. The suspension was prepared with a polyphenylmethylsiloxane (type H62C, Wacker Chemie Co.), to which 25 vol.% MoSi_2 powder (same type as in Example 1), 5 vol.% mullite, and 5 vol.% Al_4Si_3 had been added, based on the siloxane phase = 100 vol.%. The highly fluid consistency of the suspension was produced with toluene in this case. After an aging treatment at 1,500°C in air had been carried out on the pipe coated in this way, further improvement of the anchoring of the oxidation-resistant coating on the surface of the pipe was observed. Coatings produced in this way show further improvement of the long-term oxidation resistance at temperatures above 1,600°C.

Example 5

Polyphenylsiloxane (same type as in Example 3), corresponding to 100 vol.%, was treated with 20 vol.% MoSi₂ (same type as in Example 1) and with 30 vol.% of an extremely fine SiC powder (FEPA, grain size F 1200, manufactured by Lonza-Werke, Landshut) and converted to a brushable suspension by adding acetone and mixing. This suspension was applied to a plate with the dimensions 10 × 12 × 1 cm, which was composed of recrystallized SiC, by spreading it over the surface with a brush until a coating thickness of 300 μm was obtained. The coating applied in this way was converted to the finished ceramic protective coating as described in Example 3. During these treatment steps, the extremely fine SiC particles penetrated the pores, cracks, and depressions in the surface of the substrate body. This resulted in an especially smooth surface, which was well anchored in the surface of the substrate body, was resistant to oxidation up to temperatures of 1,500°C, and also showed excellent abrasion resistance.

CLAIMS

1. Abrasion-resistant surface coating, which contains a matrix glass, silicon carbide, and molybdenum disilicide and protects substrate bodies composed of silicon carbide from oxidation by oxygen, characterized by the fact that the coating consists of a material, which is formed from a mixture of a polysiloxane and molybdenum disilicide finely distributed in it by heat treatment up to a temperature of 1,700°C and still contains a fraction of molybdenum disilicide that did not react during the heat treatment.

2. Protective surface coating in accordance with Claim 1, characterized by the fact that the surface coating has a thickness of 5-500 μm .

3. Protective surface coating in accordance with Claim 1, characterized by the fact that the protective surface coating has a thickness of 30-300 μm .

4. Method of producing an abrasion-resistant surface coating, which contains at least a matrix glass, silicon carbide, and molybdenum disilicide and protects substrate bodies composed of silicon carbide from oxidation by oxygen, characterized by the fact that a suspension of a polysiloxane and molybdenum disilicide particles is prepared, this suspension is applied to the parts of the surface of the silicon carbide body that are to be protected, the body coated in this way is subjected to a first heat treatment at temperatures of up to a maximum of 400°C, the body that has been heat-treated in this way is subjected to a pyrolysis treatment in the temperature range of 1,000-1,600°C in an atmosphere that is inert with respect to oxidative effects, and, after this pyrolysis treatment, the body is subjected to a heat treatment in an oxidizing atmosphere at temperatures above 800°C.

5. Method of producing a surface coating in accordance with Claim 4, characterized by the fact that the suspension consists of a first component of polysiloxane = 100 vol.% and at least

a second component of 10-60 vol.% molybdenum disilicide added to the polysiloxane.

6. Method of producing a surface coating in accordance with Claim 4, characterized by the fact that the suspension consists of a first component of polysiloxane = 100 vol.% and at least a second component of 20-50 vol.% molybdenum disilicide added to the polysiloxane.

7. Method of producing a surface coating in accordance with any of Claims 4, 5, and 6, characterized by the fact that the suspension intended for the coating additionally contains 0-60 vol.% of substances, which form aluminum oxide or an aluminosilicate phase in at least one of the heat treatment steps.

8. Method of producing a surface coating in accordance with any of Claims 4, 5, 6, and 7, characterized by the fact that the coating suspension consisting of polysiloxane and molybdenum disilicide additionally contains 0-60 vol.% of a material from the group comprising silicon carbide and the silicides of the metals niobium, tantalum, chromium, tungsten and aluminum in finely powdered form.

9. Method of producing a surface coating in accordance with any of Claims 4, 5, 6, 7, and 8, characterized by the fact that the siloxane resin that is used produces a yield of ceramic residue of at least 70 wt.% after the thermal decomposition in accordance with the method.

10. Use of surface coatings produced in accordance with the preceding claims with respect to the method as protective coatings that are resistant to abrasion, oxidation, and high temperatures when applied to porous substrate bodies composed of silicon carbide.

11. Use in accordance with Claim 10 of surface coatings produced in accordance with the preceding claims with respect to the method at temperatures of up to 1,700°C.